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Lead Phosphate Glasses

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ABSTRACT

Measurements of optical absorption and emission spectra of Nd^{3+} in lead phosphate glasses at 295 K are compared with results reported earlier for various metaphosphate glasses. The Judd-Ofelt intensity parameters for high-lead-content phosphate glasses are the smallest observed thus far for metaphosphate glasses with divalent network modifier cations.

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INTRODUCTION

The optical absorption and emission properties of Nd^{3+} ($[\text{Xe}4f^3]$) ions in a series of alkaline earth (Mg, Ca, Sr, Ba) and other divalent (Zn, Cd) and trivalent (Al, Nd) modifier metaphosphate glasses have been described previously [1]. For the divalent alkaline earths, it was found that the Nd^{3+} spectroscopic properties varied systematically with the alkaline earth atomic number. In the case of Zn and Cd, the other divalent cation network modifiers studied, the data did not conform to the trend observed for Nd^{3+} in the alkaline earth metaphosphates. The observed differences in the behavior of the two types of cations are attributed to their different electronic structures - i.e., the divalent alkaline earths are closed shell ions of the type $\dots ns^2 p^6$ ($n = 2, 3, 4, 5$) while Zn and Cd have a noble gas configuration and an $\dots ns^2 p^6 d^{10}$ ($n = 3, 4$) outer shell.

In the present work, the earlier investigation are extended to encompass lead phosphate glasses including the lead metaphosphate composition. Divalent lead has a $6s^2$ outer shell, is easily polarized, and forms a $\text{M(II)}-\text{O}$ bond with the most covalent character [2]. As will be shown, several of the optical properties of Nd^{3+} in the metaphosphate glasses exhibit extremes when lead is the modifier cation. This observation led us to investigate the spectroscopic properties of Nd^{3+} in phosphate glasses with lead concentrations greater than that corresponding to the metaphosphate composition.

GLASS PREPARATION

Lead metaphosphate glass $\text{Pb}(\text{PO}_3)_2$ was prepared by D. Blackburn of The National Bureau of Standards, using high purity PbO and $\text{NH}_4\text{H}_2\text{PO}_4$ as starting

materials. The batches were melted in an alumina crucible in air at a temperature of about 1000°C for several hours, poured at 850°C into a steel mold, and subsequently annealed at about 400°C. It was difficult to obtain homogeneous phosphate glasses containing higher concentrations of lead by simply melting together a mixture of the two powders. As an alternative, a precipitation technique was used to prepare crystalline lead hydrogen phosphate (PbHPO_4) powder which contained an excess of phosphoric acid. This material was melted together with Nd_2O_3 in a platinum crucible at 1050°C for 5 h, poured into a spectroscopically pure graphite mold, and the glass was then annealed at 450°C for 1 h. Using this procedure, samples were prepared which had PbO concentrations near the 66 wt. % limit for glass formation [3]. The elemental ratio of phosphorous-to-lead was determined from energy dispersive x-ray analysis. To study the spectroscopic properties of Nd^{3+} , doping levels of 1 mol % Nd_2O_3 were employed.

OPTICAL PROPERTIES

Absorption and fluorescence spectra of Nd^{3+} were recorded at room temperature using apparatus techniques described previously [1]. Table I summarizes the physical and spectroscopic properties for a lead metaphosphate glass and for a higher-lead-content phosphate glass. For comparison, the extreme values measured earlier for other divalent cation metaphosphate glasses are given in the final column of the table. The modifier ion which exhibited the observed extreme value is noted in parentheses. Whereas the lead metaphosphate glass transmitted above 280 nm, the absorption edge of the higher-lead-content glass is shifted slightly to longer wavelengths with a tail that had an absorption coefficient of 6 cm^{-1} at 300 nm.

The Nd^{3+} spectra observed for lead phosphate glasses were very similar to those shown in Ref. 1, but exhibited a slight narrowing of the band widths and small changes in band intensities of transitions between J states. Intensity changes have also been observed for silicate glasses with comparable PbO content [4]. The strong covalent character of the Pb-O bond effectively reduces the ligand field at the Nd^{3+} site. The resulting small overall Stark splitting accounts for the narrower effective linewidth for the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ emission in Table I.

All of the Judd-Ofelt intensity parameters for Nd-doped lead phosphate glasses are smaller than those for the other divalent-cation metaphosphate glasses. This is a consequence of the high polarizability of Pb^{2+} and the directional nature of the Pb-O bond. The Ω_2 parameter, which is derived principally from the hypersensitive $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$ transition at ~ 580 nm, decreases with increasing PbO content and has the smallest value observed in any oxide glass. The only glasses exhibiting smaller Ω_2 values are halide containing glasses [5]; these glasses also have weak local fields and narrow linewidths.

The fluorescence decays, measured in samples containing 0.1 wt. % Nd_2O_3 to reduce nonradiative relaxation by ion-ion interactions, were nonexponential with lifetimes less than the radiative lifetime predicted from the Judd-Ofelt parameters. The difference is attributed to the presence of a small quantity of water in the glasses as evidenced by infrared absorption bands in the vicinity of $3 \mu\text{m}$ characteristic of hydroxyl groups in phosphate glasses. The predicted branching ratios for fluorescence from the $^4\text{F}_{3/2}$ state to levels of $^4\text{I}_J$ manifolds were within a few percent of the values predicted for other phosphate glasses.

CONCLUSIONS

Several of the spectroscopic properties of Nd^{3+} in lead metaphosphate glass represent extremes for metaphosphate host glasses with divalent modifier cations. The observed behavior of optical properties in high-lead-content phosphate glasses can therefore be used to tailor the host glass composition for absorption and luminescence applications [6]. Although the intensity parameters for rare earths are small, the peak cross sections are relatively large and the radiative lifetime are short because of the narrow band widths and high refractive index. The predicted nonlinear refractive index coefficient n_2 in the visible and infrared is estimated to be large, $\sim 5 \times 10^{-20} \text{ m}^2/\text{W}$, for PbO concentrations of ~ 50 mol %. Hence lead phosphate glasses are not attractive for laser applications where effects of self-focusing are detrimental.

Lead phosphate glasses containing ~ 9.0 wt. % Fe_2O_3 are also of interest as a medium for the storage of high-level nuclear wastes. Relative to borosilicate glasses, lead-iron phosphate glass has the combined advantages of greater corrosion resistance, lower processing temperature, and lower melt viscosity [3].

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TABLE I Comparison of the spectroscopic and physical properties of Nd^{3+} -doped lead phosphate and various metaphosphate ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Zn}, \text{Cd}$) glasses at 295 K. The extreme values measured for metaphosphate glasses are given.

Glass	$1 \text{ Nd}_2\text{O}_3$ - $49\text{PbO}-50\text{P}_2\text{O}_5$	$1.7\text{Nd}_2\text{O}_3$ - $53.6\text{PbO}-44.7\text{P}_2\text{O}_5$	$1\text{Nd}_2\text{O}_3$ - $49\text{MO}-50\text{P}_2\text{O}_5$
Physical Properties:			
Density (g/cm^3)	4.56	5.07	2.48(Mg)-3.83(Cd)
Refractive index n_D	1.71	1.75	1.50(Mg)-1.62(Cd)
Abbe number ν_D	61	58	66(Mg)-56(Cd)
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ Fluorescence:			
Peak cross section (pm^2)	3.5 ± 0.1	3.6 ± 0.1	2.4(Mg)-3.9(Ba)
Peak wavelength (nm)	1054	1054	1055(Cd)-1056(Ba)
Effective linewidth (nm)	25.2	25.1	28.5(Ba)-33.9(Mg)
Radiative lifetime (μs)	320	300	290(Ba)-430(Mg)
Judd-Ofelt Intensity Parameters:			
$\Omega_2(\text{pm}^2)$	2.6 ± 0.2	2.0 ± 0.2	3.9(Cd)-5.3(Mg)
$\Omega_4(\text{pm}^2)$	3.5 ± 0.3	3.6 ± 0.3	4.2(Cd)-5.4(Ba)
$\Omega_6(\text{pm}^2)$	4.3 ± 0.1	4.2 ± 0.1	4.3(Mg)-5.6(Ba)